

Quadrupolar Glass State in para-hydrogen and ortho-deuterium under pressure.

T.I.Schelkacheva.

*Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk 142092,
Moscow Region, Russia*

e-mail: schelk@hppi.troitsk.ru

The main features of the possible quadrupolar glass state in ortho-deuterium and para-hydrogen under high pressure are predicted and considered in replica-symmetric approximation in analogy with glassy behavior of diluted ortho-hydrogen at low pressures. The quadrupolar model with $J = 2$ is suggested. The orientational order and glass regime grow continuously on cooling just as it is in the case of ortho-para hydrogen mixtures at zero pressure.

The structure of high pressure phases of solid hydrogen has been widely investigated recently (e.g. [1, 2, 3]). At low pressures, the centers of para-hydrogen and ortho-deuterium molecules occupy the lattice sites of the hcp structure. The molecules are in spherically symmetric states (phase I or SP). Between 28 GPa for o-D₂ and 110 GPa for p-H₂ and ~150 GPa the molecules become orientationally ordered in broken-symmetry phase II (BS).

High pressure breaks the rotational symmetry of the $J=0$ solids. The ordering occurs even in the systems of para-hydrogen and ortho-deuterium molecules because of mixing of higher order J levels with the ground state $J = 0$ as a result of the increase of the intermolecular interactions at high pressures [1,2]. The anisotropic interaction between two molecules is

dominated at low pressures [5] by electrostatic quadrupole-quadrupole (EQQ) interaction, which plays a major role below 100 Gpa [1, 4]. However it is necessary to take into account other anisotropic interactions to understand the results of precise experiments (e.g. Raman scattering [1]).

The purpose of this article is to show the possibility of orientational glass state in solid p-H₂ and o-D₂ under pressure. Only the main features of this phenomenon will be taken into account. The $J = 0 \rightarrow J = 2$ transitions take place as a result of the pressure increasing. In this case the $J=2$ molecules may be randomly distributed on a close packed lattice. It has been indicated in [2, 6] that rotational disorder under pressure may be frozen. The molecules with $J=0$ are spherically symmetric, have no electric quadrupole moment and play the role of dilutant.

So we can consider the quadrupolar glass state in analogy with glassy behavior of diluted o-H₂ and p-D₂ at low temperatures and pressures. In this case only the ortho-hydrogen and para-deuterium molecular species are orientable. They have orbital angular momentum $J = 1$. The ordered state is characterized by a long-range orientational order at high ortho-H₂ and para-D₂ concentrations [5]. However, for concentrations less than approximately 55%, measurements show no evidence of orientational phase transition. Instead, NMR experiments have been interpreted in terms of freezing of the the orientational degrees of freedom [7, 5]. This state is so called quadrupolar glass.

The EQQ interaction can bring about orientational glass state at high pressure in p-H₂ and o-D₂. The rough estimation of $0 \rightarrow 2$ transition probability α can be done [4, 6] using quantum mechanical perturbation theory because the main anisotropic part (EQQ) of the intermolecular interaction is small [5]. We have $\alpha = 4 \times 10^{-4}$ for D₂ and $\alpha = 6 \times 10^{-5}$ for H₂ at zero pressure. The probability to find a $J = 2$ molecule increases strongly with pressure; $\alpha = 0.1$ at 40 Gpa for D₂ and 150 Gpa for H₂ and $\alpha = 0.4$ for

D₂ at 150 Gpa. It is possible that an intermediate range of α exists where a quadrupolar glass occurs.

Let us consider the system of particles on lattice sites i, j with the truncated EQQ Hamiltonian

$$H = -\frac{1}{2} \sum_{i \neq j} J_{ij} Q_i Q_j \quad (1)$$

where the quadrupole component $Q = \frac{1}{2} \left[3 \left(\frac{z}{r} \right)^2 - 1 \right]$ can be replaced by

equivalent operator with the same matrix elements $\hat{Q} \sim [3J_z^2 - J(J+1)]$ in the space $J = \text{const}$. $Sp \hat{Q} = 0$.

Quadrupolar glass freezing in mixtures of ortho- and para-hydrogen has been considered [8] with

$$Q = 3J_z^2 - 2, J_z = 1, 0, -1 \text{ and } J = 1. \quad (2)$$

This model describes well the zero pressure experiments on ortho- para mixtures even in replica-symmetric approach.

Now the Hamiltonian (1) will be examined on the condition $J = 2$ and $J_z = 0, 1, -1, 2, -2$.

$$Q = \frac{1}{3} [3J_z^2 - 6], \quad (3)$$

J_{ij} are random exchange interactions with Gaussian probability distribution

$$P(J_{ij}) = \frac{1}{\sqrt{2\pi} J} \exp \left[-\frac{(J_{ij} - J_0)^2}{2 J^2} \right].$$

The scaling $J = \tilde{J}/\sqrt{N}$, $J_0 = \tilde{J}_0/N$ ensures as usual sensible thermodynamic limit. The multiplier 1/3 in (3) is used for simplicity.

Using replica method the free energy is obtained in the form

$$\begin{aligned} \langle F \rangle_J / NkT = & -\lim_{n \rightarrow 0} \frac{1}{n} \max \left\{ -\sum_{\alpha} \frac{(x^{\alpha})^2}{2} - \sum_{\alpha} \frac{(w^{\alpha})^2}{2} - \sum_{\alpha > \beta} \frac{(y^{\alpha, \beta})^2}{2} + \right. \\ & \left. + \ln Tr_{\{Q^{\alpha}\}} \exp \left[\sum_{\alpha} x^{\alpha} \sqrt{\frac{\tilde{J}_0}{kT}} Q^{\alpha} + \sum_{\alpha} w^{\alpha} \frac{1}{\sqrt{2}} t (Q^{\alpha})^2 + \sum_{\alpha > \beta} y^{\alpha, \beta} t Q^{\alpha} Q^{\beta} \right] \right\}. \end{aligned}$$

Extreme conditions for the free energy give the equations for order parameters

$$\begin{aligned} m_{\alpha} = (x^{\alpha})^{extr} / \sqrt{\frac{\tilde{J}_0}{kT}} = \langle Q^{\alpha} \rangle_{eff}; \quad q^{\alpha, \beta} = (y^{\alpha, \beta})^{extr} / t = \langle Q^{\alpha} Q^{\beta} \rangle_{eff}; \\ p^{\alpha} = (w^{\alpha})^{extr} \sqrt{2} / t = \langle (Q^{\alpha})^2 \rangle_{eff}; \end{aligned}$$

where $t = \tilde{J}/kT$ and averaging is performed with the effective Hamiltonian

$$-H_{eff} = \sum_{\alpha} \frac{\tilde{J}_0}{kT} m_{\alpha} Q^{\alpha} + \sum_{\alpha} \frac{t^2}{2} p^{\alpha} (Q^{\alpha})^2 + \sum_{\alpha > \beta} t^2 q^{\alpha, \beta} Q^{\alpha} Q^{\beta}$$

Free energy and order parameters in the replica-symmetric [9] case become

$$F = -NkT \left\{ -\left(\frac{\tilde{J}_0}{kT} \right) \frac{m^2}{2} + t^2 \frac{q^2}{4} - t^2 \frac{p^2}{4} + \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} \exp\left(-\frac{z^2}{2}\right) \ln Sp[\exp(\theta_2 Q + \theta_1 Q^2)] \right\}. \quad (4)$$

$$\text{Here } \theta_1 = t^2 \frac{p-q}{2} \text{ and } \theta_2 = zt\sqrt{q} + m\left(\frac{\tilde{J}_0}{kT}\right).$$

Order parameters are: m – quadrupolar order parameter (analog of magnetic moment in spin glasses), q – glass order parameter and p – auxiliary order parameter.

$$\begin{aligned}
m &= \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} \exp\left(-\frac{z^2}{2}\right) \frac{Sp[Q \exp(\theta_2 Q + \theta_1 Q^2)]}{Sp[\exp(\theta_2 Q + \theta_1 Q^2)]} = \\
&= \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} \exp\left(-\frac{z^2}{2}\right) 2 \left\{ \frac{\exp(4\theta_1)[- \exp(-2\theta_2) + \exp(2\theta_2)] - \exp(-\theta_2\theta_1)}{\exp(4\theta_1)[\exp(-2\theta_2) + 2 \exp(2\theta_2)] + 2 \exp(-\theta_2\theta_1)} \right\}, \quad (5)
\end{aligned}$$

$$\begin{aligned}
q &= \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} \exp\left(-\frac{z^2}{2}\right) \left\{ \frac{Sp[Q \exp(\theta_2 Q + \theta_1 Q^2)]}{Sp[\exp(\theta_2 Q + \theta_1 Q^2)]} \right\}^2 = \\
&= \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} \exp\left(-\frac{z^2}{2}\right) 4 \left\{ \frac{\exp(4\theta_1)[- \exp(-2\theta_2) + \exp(2\theta_2)] - \exp(-\theta_2\theta_1)}{\exp(4\theta_1)[\exp(-2\theta_2) + 2 \exp(2\theta_2)] + 2 \exp(-\theta_2\theta_1)} \right\}^2, \quad (6)
\end{aligned}$$

$$\begin{aligned}
p &= \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} \exp\left(-\frac{z^2}{2}\right) \frac{Sp[Q^2 \exp(\theta_2 Q + \theta_1 Q^2)]}{Sp[\exp(\theta_2 Q + \theta_1 Q^2)]} = \\
&= \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} \exp\left(-\frac{z^2}{2}\right) 2 \left\{ \frac{2 \exp(4\theta_1)[\exp(-2\theta_2) + 2 \exp(2\theta_2)] + \exp(-\theta_2\theta_1)}{\exp(4\theta_1)[\exp(-2\theta_2) + 2 \exp(2\theta_2)] + 2 \exp(-\theta_2\theta_1)} \right\}. \quad (7)
\end{aligned}$$

The temperature dependence of order parameters obtained from (5) – (7) is represented in figures 1 - 3. There is no trivial solution $m = 0$, $q = 0$ at finite temperature because $SpQ^3 \neq 0$. The orientational order and glass regime grow continuously on cooling just as it is in the case of the Hamiltonian (1) – (2) describing the ortho-para hydrogen mixtures at zero pressure [8]. The quadrupolar long range order is present for $T > 0$ even if $J_0 = 0$. In the pure case ($\tilde{J} = 0, \tilde{J}_0 \neq 0$) we have from (5) – (6) $q^{1/2} = m$.

It is easy to see from (2) that $Q^2 = 2 - Q$. So the equation for p is not independent and $p = 2 - m$. There is no similar expression for Q^2 from (3) and for order parameter p here.

Using the equation (4) for the free energy the heat capacity can be written in the form

$$\frac{C_v}{kN} = \frac{d}{d(kT/\tilde{J})} \left\{ \left(\frac{\tilde{J}}{kT} \right) \frac{(q^2 - p^2)}{2} \right\} - \left(\frac{\tilde{J}_0}{\tilde{J}} \right) m \frac{dm}{d(kT/\tilde{J})}. \quad (8)$$

Specific heat as a function of (kT/\tilde{J}) calculated from (8) for the four cases of (\tilde{J}_0/\tilde{J}) is shown in figure 4. The dependence of C_v on the temperature is smooth as in ortho-para mixtures at zero pressure.

In conclusion, the main features of the random quadrupolar system (1), (3) are considered in the replica-symmetric mean-field approximation. This system with $J = 2$ has not been considered earlier. The possible realization of the quadrupolar glass state under high pressure in ortho-deuterium and para-hydrogen is predicted.

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References

1. A.F.Goncharov, M.A.Strzhemechny, H.K.Mao, R.J.Hemly. Phys. Rev. B **63** (2001) 064304.
2. H.K.Mao, R.J.Hemly. Rev. Mod. Phys. **66** (1994) 671.
3. Paul Loubeyre, Florent Occelli and Rene LeToullec. Nature **416** (2002) 613.
4. T.I.Schelkacheva. Phys. Lett. A **239** (1998) 397.
5. I.F. Silvera. Rev. Mod. Phys. **52** (1980) 393.
6. E.A.Lutchinskaia, E.E.Tareyeva, in: The High Pressure Effects in Materials (Kiev, 1986) p, 21.
7. N.S.Sullivan, M.Devoret, B.P.Cowan, C.Urbina. Phys. Rev. B **17** (1978) 5016.
8. E.A.Lutchinskaia, V.N.Ryzhov, E.E.Tareyeva, J. Phys. C: Solid State Phys. **17** (1984) L665.
9. S. Kirkpatrick, D.Sherrington. Phys. Rev. B **17** (1978) 4384.

Fig.1. Order parameters for the case $\tilde{J}_0/\tilde{J} = 0$.

Fig.2. Order parameters for the case $\tilde{J}_0/\tilde{J} = 1$.

Fig.3. Order parameters for the case $\tilde{J}_0/\tilde{J} = 2.5$.

Fig.4. Specific heat as a function of (kT/\tilde{J}) for the cases

$\tilde{J}_0/\tilde{J} = 0; \tilde{J}_0/\tilde{J} = 1; \tilde{J}_0/\tilde{J} = 1.4; \tilde{J}_0/\tilde{J} = 2.5$

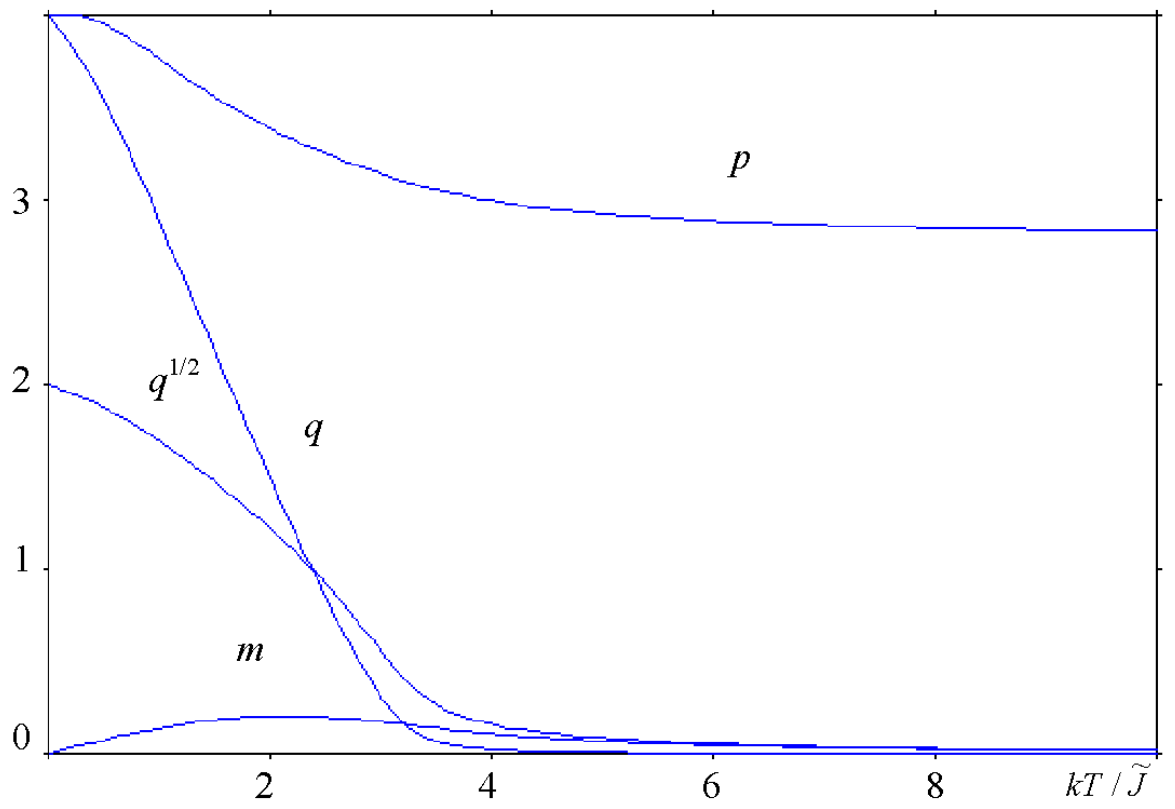


Fig. 1

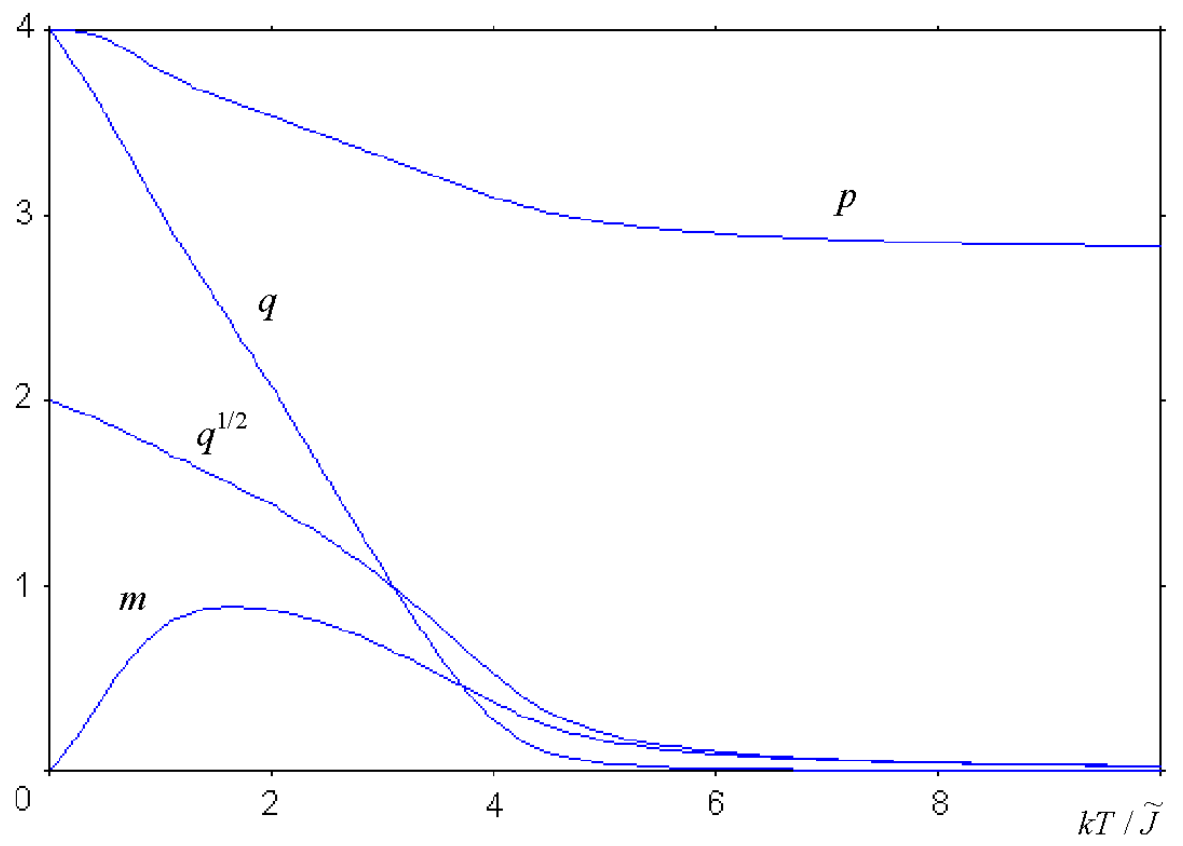


Fig. 2

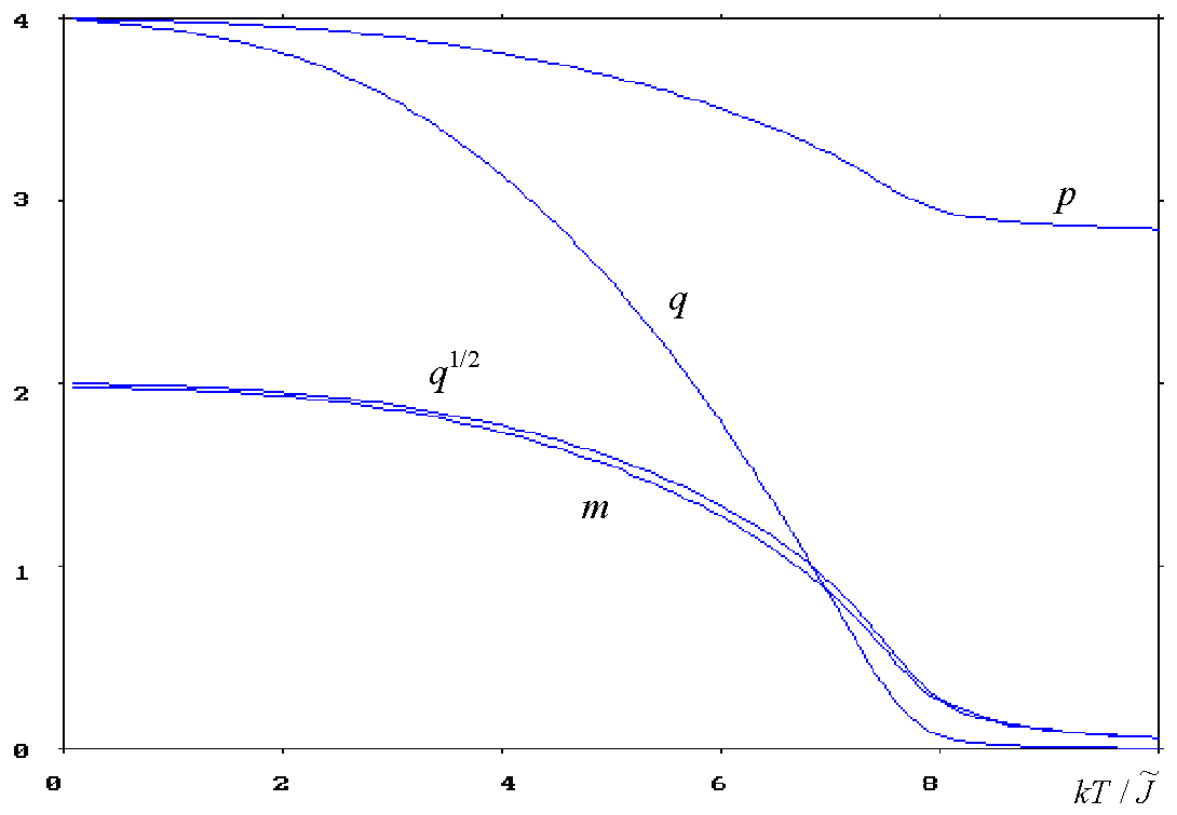


Fig. 3

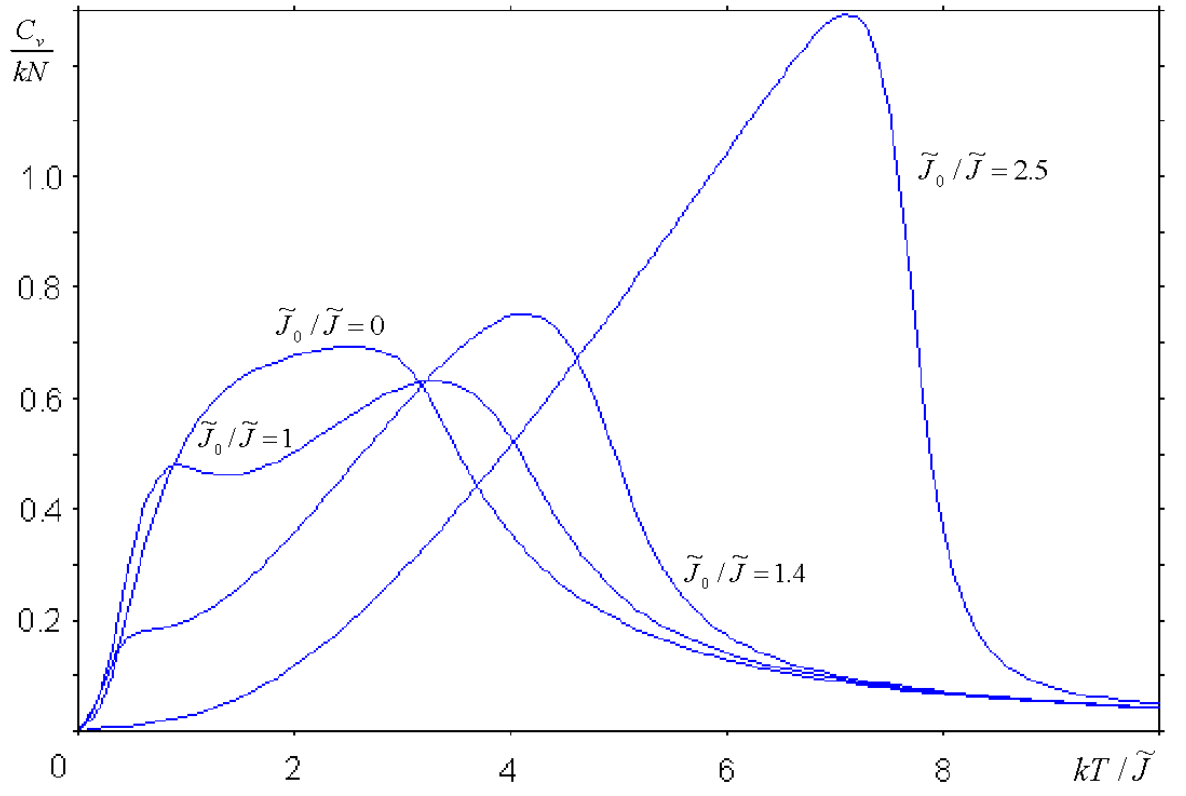


Fig. 4